THE CRYSTAL STRUCTURE OF A SODIUM-CALCIUM VARIETY OF METAHEWETTITE

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ABSTRACT

A structure is proposed for the anhydrous and hydrated forms of a sodium-calcium variety of metahewettite (Harvard 95445) from Montrose County, Colorado, having the probable composition $NaCa_{0.5}O.3V_2O_5$ and $NaCa_{0.5}O.3V_2O_5.2H_2O$, respectively. Owing to the unsuitable quality of the only available material, it was necessary to treat small fibre bundles as single crystals. The accuracy attained in the collection of two-dimensional data, therefore, was unavoidably lower than normally would be tolerated, but refinement reduced R for the $\{h0l\}$ zones of the anhydrous and hydrated specimens, and for the $\{hk0\}$ zone of the latter, to reasonable values, and, with a few exceptions, interatomic distances are acceptable. The structures are very much alike and are similar to that of $\gamma Li_{1+x}V_3O_6$ except that Na (and $Ca_{0.5}$) occupy tetrahedral, instead of octahedral, sites, in the anhydrous specimen, and there is trigonal bipyramidal co-ordination of O around each of the three non-equivalent V, instead of around one only. The trigonal bipyramids share edges to form zigzag chains along the direction of y, and the chains along the edges of the unit cell are joined through corners into spiral tubes about the 2_1 axes perpendicular to $y = 0$. The cations (and the water molecules in the hydrated material) are situated between the chains of trigonal bipyramids with $z = \frac{1}{2}$ as the median plane.

INTRODUCTION

Hillebrand, Merwin & Wright (1914) analyzed a mahogany-red oxidation product of patronite from Minasragra, Cerro de Pasco, Peru, briefly described earlier by Hewett (1910). The mineral was identified as a hydrous calcium vanadate, $CaO.3V_2O_5.9H_2O$ and was named "hewettite." Seemingly identical minerals from Paradox Valley, Montrose County, Colorado, and from Thompson's in eastern Utah, were found to have the same composition but appeared to exhibit different dehydration characteristics and minor differences in optical behaviour and morphological appearance. On this basis the North American minerals were considered to represent an isomer of hewettite which was given the name "metahewettite." Both hewettite and metahewettite lose $6H_2O$ per formula unit on dehydration over sulphuric acid at room temperature (Hillebrand, Merwin & Wright, 1914). An x-ray diffraction powder study at room temperature of wet and dry samples of several specimens variously labelled "hewettite" and "metahewettite" (Barnes, 1955), however, indicated that the two minerals must be structurally identical, and that the name metahewettite should be discarded unless retained to designate one of the hydrate phases. It has been suggested (Weeks in Ross, 1959) that "hewettite" be reserved for the fully-hydrated mineral, $CaO.3V_2O_5.9H_2O$, and that "metahewettite" be employed for the trihydrate, $CaO.3V_2O_5.3H_2O$, and the two names are used in this sense throughout the remainder of the present paper. Separate names for the two hydrates are in keeping with preliminary structural studies (Qurashi, 1961), and with current usage, as in the case of "rossite" for $CaO.V_2O_5.4H_2O$ and "metarossite" for $CaO.V_2O_5.2H_2O$ (Foshag & Hess, 1927; Kelsey & Barnes, 1960, 1961).

A single-crystal *x*-ray investigation of a "metahewettite" from the Cactus Rat mine, Yellow Cat District, Grand County, Utah (Harvard 98019) indicated monoclinic symmetry with a 2_1 axis, but only one formula unit of $CaO.3V_2O_5.3H_2O$ per cell, which suggested that the screw axis must be due to some structural pseudo-symmetry (Barnes & Qurashi, 1952). One of the peaks on the *h0l* electron-density map, however, was somewhat low for V but was of about the right height for Na, while the peak tentatively attributed to Ca could be assigned to V (Barnes, 1955). This specimen (Harvard 98019) was, in fact, identified (Barnes, 1955) as the sodium analogue of metahewettite, first reported from the Cactus Rat mine by Weeks & Thompson (1954). The sodium analogue, unlike metahewettite and hewettite, is not sensitive to hydration or dehydration at room temperature, and its powder pattern resembles that of metahewettite more closely than that of hewettite.

Another mineral specimen which appears to be a sodium-calcium variety of metahewettite is represented by a Harvard specimen, 95445. This consists of long, red blades, closely resembling an authentic hewettite-metahewettite specimen from the Jo Dandy mine, Montrose County, Colorado (U.S.G.S., MNG/4/49), together with some darker-red, fine-grained material, on, and impregnating, sepiolite with quartz. The locality of origin unfortunately is not known more specifically than Montrose County, Colorado. A spectrochemical test showed Na, Ca, and V to be the only cations present (there was no K, Mg, or Al). A flame-photometer test gave $3.7\pm0.4\%$ Na (the sample selected was too small for a separate Ca estimation), whereas a duplicate test of the sodium analogue of metahewettite (Harvard 98019) gave $6.5\pm0.7\%$ Na, which is in satisfactory agreement with 6.9% Na calculated for $Na_2O.3V_2O_5.3H_2O$. Thus, the Harvard specimen 95445 appears to be a mixed variety of metahewettite with about 50% each of Na and Ca. A micro-water determination on 15 mg (7 hours at 140° C over P_2O_5 at a pressure of 0.02mm Hg) resulted in a loss of weight of 6.14%, or 2.196 mole H_2O

per mole $NaCa_{0.5}V_6O_{16}$. The composition of this Na-Ca variety, therefore, may be represented as $NaCa_{0.5}O \cdot 3V_2O_5 \cdot 2H_2O$, and the specimen contains 3.6% Na, in very good agreement with the flame-photometer estimation. That this specimen does not simply represent a mixture of metahewettite and its sodium analogue is borne out by the following considerations. The powder patterns of six samples selected at random (four of the long blades, and two of the fine-grained material) are identical with the exception of a few lines due almost entirely to sepiolite and quartz in those of the granular samples. Although there is some coincidence of lines, the powder pattern is not the same as those of metahewettite or its sodium analogue, either separately or combined, and it shows no change after wetting or drying the sample at room temperature, as should be the case if metahewettite were present. Similarly, after complete dehydration at 140° C, the powder pattern again cannot be accounted for in terms of those of metahewettite or the sodium analogue after their complete dehydration; it is of interest to note that the powder patterns of the two latter are almost identical except for slightly different values of 2θ which may be accounted for by an increase in the lattice parameters when Ca is present instead of Na.

Appropriate conditions for the synthesis of hewettites and metahewettites have been discussed by Marvin (1955) and by Evans & Garrels (1958). Several alkali metal and alkaline earth vanadates of various degrees of hydration, in which the alkali-oxide to V_2O_5 ratio (1:3) is the same as in metahewettite, have been prepared in the course of studies of synthetic vanadates by von Hauer (1860), Norblad (1873), Manasse (1887), Ditte (1888), and Guiter (1941). There is no difficulty in preparing metahewettite or its sodium analogue separately from aqueous solutions of *p*H between about 2.8 and 5.5. Attempts to synthesize a substance identical with Harvard 95445, however, have so far been unsuccessful. All products obtained from polyvanadate solutions of suitable *p*H and containing sodium and calcium ions in the ratios Na:Ca = 9:1, 8:2, 7:3, . . . 3:7, 2:8, 1:9 gave powder patterns as prepared, after wetting, and after prolonged drying at room temperature, which are indistinguishable from that of the pure sodium analogue of metahewettite.

Some preliminary structural work has been carried out on hewettite, metahewettite, and the sodium analogue of the latter (Barnes & Qurashi, 1952; Qurashi, 1961), and Ross (1959) has reported values for *a* and *b* of hewettite (probably metahewettite) specimens from the Hummer mine, Jo Dandy group, Montrose County, Colorado, and from the Cactus Rat mine, Utah, and of the sodium analogue (also from the Cactus Rat mine) based on electron diffraction photographs.

The present paper is concerned with an attempt to solve the crystal structure of the mixed Na-Ca metahewettite represented by Harvard 95445. The extreme difficulties encountered in single-crystal work on the metahewettites have been mentioned elsewhere (Barnes & Qurashi, 1952). The Na-Ca variety suffers from the same disadvantages of silky fibres of very small cross-section, elongated along [010], and grouped into bundles which frequently exhibit a helical twist. No single fibres with a diameter remotely approaching a feasible size could be located. Because the fibres occur with their (001) faces nearly parallel to one another, it was decided to treat a small bundle as a single crystal, which is valid providing the cross-section does not exceed about $50 \times 10\mu$. Lengths exceeding 500μ could not be employed because of a tendency for longer bundles to bend under their own weight. It was impossible, therefore, to collect intensity data with the usual degree of accuracy normally attained with photographic recording.

DATA COLLECTION

Dehydration of a sample of $NaCa_{0.5}V_6O_{16}.2H_2O$ left the fibres intact so that it was possible to collect data from specimens of both the hydrated and the anhydrous forms. Because of the fibrous nature of both types of material, however, Weissenberg techniques were impractical; with the long [010] fibre axis as rotation axis the spots were drawn out into long streaks extending almost entirely across the films. Precession photographs along [001] of the hydrated specimen, taken with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and exposure times of up to 200 hours, provided useful data for the $hk0$ reflections for which $(\sin\theta)/\lambda \leqslant 0.45$ Å^{-1}. The $h0l$ data were obtained from zero-layer rotation and oscillation photographs with [010] as the rotation axis; thirty-six 10° oscillation photographs with 5° overlap between successive exposures were obtained with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and exposure times of 20 hours each, thus covering a range of 2θ from 0° to 180°. Observable $h0l$ and $\bar{h}0l$ reflections were recorded for which $(\sin\theta)/\lambda \leqslant 0.35$ Å^{-1}. A total of 1551 intensity measurements were made on these oscillation films, the large number arising from the fact that both the left- and right-hand sides of the films were included and the same reflections were observed several times owing to the overlapping of successive photographs and to the polycrystalline nature of the specimen.

Precession photographs along [001] of the anhydrous sample were too weak, even after very long exposures, to be of any value except to show that systematic extinctions probably were the same as for the hydrated specimen and that the relative intensities of corresponding reflections from the two types of material were very similar. Data collection for the dehydrated sample, therefore, was confined to oscillation photographs about [010]. These were taken with Cu $K\alpha$ radiation at 5° intervals, without overlap, over the 2θ range from 0° to 360°; exposure times were 24 hours each. The number of reflections measured was 3411 and $(\sin \theta)/\lambda \leqslant 0.35$ Å^{-1}.

Indexing the oscillation photographs was accomplished in the usual way (*e.g.*, Henry, Lipson & Wooster, 1951) except that the reciprocal lattice points were replaced by short arcs corresponding to the effect of the helical twist in the fibre bundles. Intensities were estimated visually by comparison with a calibrated strip prepared by the rotating-sector method. The appropriate *L.p.* corrections were applied but absorption was ignored, even in the case of Cu radiation, because of the very small diameter of the specimens (μ(Cu $K\alpha$) = 336 cm^{-1}; μ(Mo $K\alpha$) = 39 cm^{-1}).

UNIT CELL AND SPACE GROUP DATA

In the case of the hydrated sample, the lattice constants were obtained from the precession, rotation and oscillation photographs. The only systematic extinctions were $0k0$ when $k = 2n + 1$ (specifically the 010 and 030 reflections). The density was estimated by flotation in binary solutions of methylene iodide and carbon tetrachloride while bromoform and benzene were employed for the dehydrated material. In the case of the dehydrated sample, the lattice constants were obtained from the rotation and oscillation photographs only, because of the extreme weakness of the [001] precession photographs. The close similarity of the last with the corresponding precession photograph of the hydrated sample, and particularly the absence of the 010 and 030 reflections, however, suggested that the space groups of the two samples probably were the same and that the structures must be very much alike. Both specimens are monoclinic and the orientation chosen was that with b as the unique axis and $c < a$. The unit cell and space group data are shown in Table 1.

TABLE 1. UNIT CELL AND SPACE GROUP DATA

	$NaCa_{0.5}V_6O_{16}\cdot 2H_2O$	$NaCa_{0.5}V_6O_{16}$
a (Å)	12.26	12.28
b (Å)	3.58	3.60
c (Å)	8.11	8.00
β	92° 30′	96° 15′
S.G.	$P2_1$ or $P2_1/m$	$P2_1$ or $P2_1/m$
D (gm/ml)		
obs.	2.89	$\gtrsim 2.80$
calc.	2.99	2.86
Z	1	1

Electron diffraction photographs of the normal sample, kindly taken by Dr. Malcolm Ross, gave $a = 12.24$ Å and $b = 3.61_0$ Å, in good agreement with the corresponding data of Table 1.

STRUCTURE DETERMINATION

The determination of the structures of the hydrated and the anhydrous samples was commenced with the $h0l$ data for the latter, partly because the largest number of measurements was made for this zone, and partly because of the absence of the H_2O molecules. The Patterson function was calculated and the resulting map was almost identical with that published by Wadsley (1957, Fig. 1) for the lithium vanadium bronze, $\gamma Li_{1+x}V_3O_8$. A set of x, z co-ordinates for all V and O atoms was derived from the Patterson projection, and structure factors were calculated with the use of atomic scattering factors for V^0 given by Qurashi (1954) and for O^{-1} given by Berghuis *et al.* (1955), together with an overall isotropic temperature factor with $B = 3.0$ Å^2. A Fourier synthesis produced an electron density map ($\frac{1}{2}$ cell) which showed a peak at $x \sim \frac{1}{3}$, $z \sim \frac{1}{2}$ of height slightly greater than any of those corresponding to a single O; this peak was accepted as representing Na. There was, however, no indication of a peak in a one-fold position corresponding to a possible Ca site; such a peak would be expected to have a height more than twice that of one due to an oxygen atom. If the composition of the specimen is correctly expressed as $NaCa_{0.5}V_6O_{16}$, this result suggests that Na and Ca are indistinguishable in the present structure investigation, because $f_0(\text{Na}) = 11$ is almost equal to $f_0(\frac{1}{2}\text{Ca}) = 10$, and that Na and $\frac{1}{2}$Ca, therefore, may occupy equal numbers of the same two-fold positions. Refinement by $(F_o\text{-}F_c)$-syntheses, therefore, was carried out in terms of $Na_2V_6O_{16}$, and with atomic scattering factors for Na^{+1} given by Berghuis *et al.* (1955). The final electron density and difference maps are shown in Fig. 1. The final R-factors are 0.17 for the observed reflections only (omitting the three strongest reflections), 0.15 when the $|F_o|$'s for these three reflections are replaced by the corresponding $|F_c|$ values, and 0.21 when the unobserved reflections (assuming $|F_o| = 0$) are then included. For these data, as well as for those collected with the normal sample, values of $|F_o|$ for the strongest reflections generally were much lower than corresponding values of $|F_c|$ owing to somewhat restricted upper limits for $|F_o|$; this is believed to be due essentially to the use of single, and not multiple, films, and to the polycrystalline nature of the material from which the data were collected. Substitution of $|F_c|$ for $|F_o|$ values, however, only had the effect of increasing the electron densities corresponding to the vanadium atoms, and had virtually no

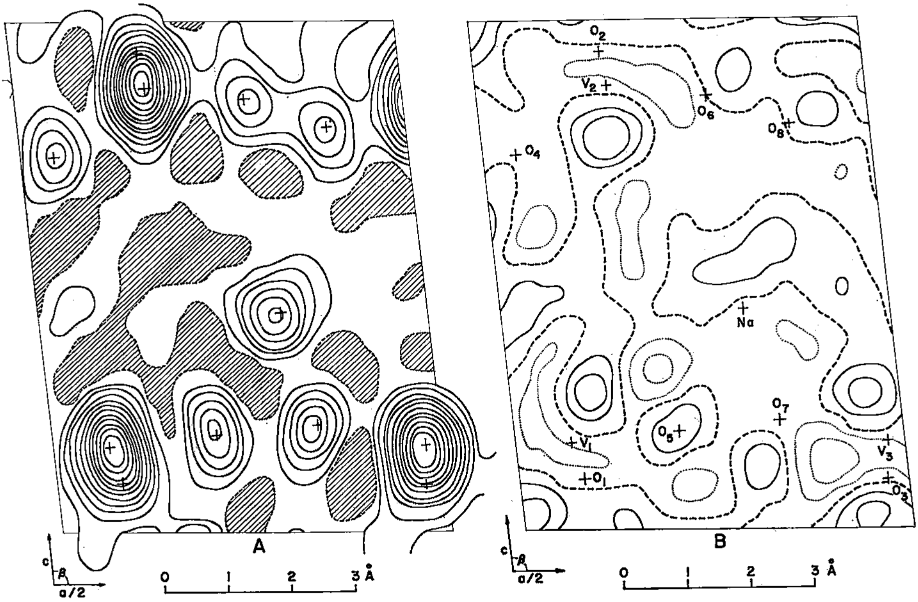

FIG. 1. $Na_2V_6O_{16}$: (A) final electron-density projection along [010] with contours at intervals of 2 $e.Å^{-2}$, and negative areas shaded; (B) final $(F_o$-$F_c)$-synthesis projected along [010] with contours at intervals of 1 $e.Å^{-2}$; zero contour broken, and negative contours dotted.

effect on the heights of the other peaks. Values of $|F_o|$ and F_c for the $\{h0l\}$ zone of $Na_2V_6O_{16}$ (where Na_2 is to be considered as probably $NaCa_{0.5}$) are listed in Table 2. Final values for the fractional atomic co-ordinates (assuming $y = \frac{1}{4}$ or $\frac{3}{4}$ for all atoms in $P2_1/m$, by analogy with $\gamma Li_{1+x}V_3O_8$) are given in Table 3.

The $hk0$ data from the [001] precession photographs were employed to obtain the electron density projection along [001] of the hydrated specimen. The x, y co-ordinates of Table 1 were adopted for the first Fourier synthesis, and structure factors were calculated with the same atomic scattering factors and general isotropic temperature factor as for the anhydrous sample, and refinement was carried out by successive Fourier and difference syntheses. Although progress was hampered by the small number of observed reflections and by serious overlapping of atoms in this projection, indications of an additional oxygen peak corresponding to the H_2O molecule appeared in the electron density maps. The final electron density and difference maps for this zone are shown in Fig. 2. The final R-factors are 0.22 for the observed reflections only (omitting the two strongest reflections), 0.13 when the $|F_o|$'s for these two reflec-

TABLE 2. STRUCTURE FACTOR DATA FOR THE $\{h0l\}$ ZONE OF $NaCa_{0.5}V_6O_{16}$ (F_c for $Na_2V_6O_{16}$ ($B = 3.0$ Å^2))

$h0l$	$\lvert F_o \rvert$	F_c	$h0l$	$\lvert F_o \rvert$	F_c	$h0l$	$\lvert F_o \rvert$	F_c
001	>43.6	116.0	500	44.4	−37.4	$\bar{3}01$	36.8	−34.4
002	49.9	−59.6	501	51.5	−44.5	$\bar{3}02$	56.8	51.7
003	>54.1	−117.1	502	62.1	−66.8	$\bar{3}03$	46.0	48.9
004	27.9	−47.9	503	<15.8	−5.3	$\bar{3}04$	25.6	26.3
005	25.8	16.8	504	27.7	25.5	$\bar{3}05$	<16.6	−14.9
100	<5.6	9.7	600	36.2	31.8	$\bar{4}01$	31.3	26.2
101	14.8	11.1	601	35.9	24.0	$\bar{4}02$	27.0	19.2
102	27.0	28.2	602	<15.8	5.4	$\bar{4}03$	30.5	29.5
103	20.6	19.0	603	<17.1	−2.2	$\bar{4}04$	18.9	−16.8
104	22.6	22.7	700	19.0	−29.7	$\bar{4}05$	<17.0	1.0
105	28.8	−28.7	701	22.6	−24.2	$\bar{5}01$	50.5	40.5
200	33.5	25.9	702	33.7	31.6	$\bar{5}02$	67.6	67.4
201	28.3	30.3	703	25.6	29.2	$\bar{5}03$	58.0	58.5
202	32.3	−34.6	800	40.4	−41.0	$\bar{5}04$	<16.4	4.5
203	<12.5	8.2	801	49.5	49.0	$\bar{5}05$	25.2	−41.6
204	18.1	10.9	802	56.5	52.3	$\bar{6}01$	<14.3	−4.1
205	<17.2	15.4	900	22.8	−33.1	$\bar{6}02$	<15.0	13.1
300	40.8	−39.8	$\bar{1}01$	20.4	20.3	$\bar{6}03$	19.7	−17.3
301	>65.0	−92.6	$\bar{1}02$	26.7	−24.9	$\bar{6}04$	24.6	−11.6
302	41.2	−61.2	$\bar{1}03$	<11.8	−3.5	$\bar{7}01$	15.6	−9.9
303	<13.5	3.2	$\bar{1}04$	37.8	−36.3	$\bar{7}02$	19.7	19.1
304	27.0	43.8	$\bar{1}05$	<16.0	−6.7	$\bar{7}03$	29.5	18.1
305	25.2	43.2	$\bar{2}01$	23.5	18.5	$\bar{7}04$	25.7	−25.5
400	<10.9	2.2	$\bar{2}02$	20.2	−24.1	$\bar{8}01$	84.3	−71.0
401	34.9	−33.2	$\bar{2}03$	21.0	−40.1	$\bar{8}02$	55.5	−56.6
402	28.5	−31.5	$\bar{2}04$	<14.3	−13.4	$\bar{8}03$	28.9	13.3
403	35.5	−38.2	$\bar{2}05$	<16.2	−9.1	$\bar{9}01$	22.6	−20.8
404	<16.5	12.3						

TABLE 3. FRACTIONAL CO-ORDINATES OF ATOMS IN $Na_2V_6O_{16}$ (where Na_2 probably should be $NaCa_{0.5}$)

Atom	x	y	z
V_1	0.072	1/4	0.169
V_2	0.830	1/4	0.130
V_3	0.523	1/4	0.830
Na	0.310	1/4	0.432
O_1	0.917	1/4	0.902
O_2	0.165	1/4	0.938
O_3	0.471	1/4	0.094
O_4	0.957	1/4	0.265
O_5	0.210	1/4	0.191
O_6	0.705	1/4	0.152
O_7	0.659	1/4	0.789
O_8	0.396	1/4	0.793

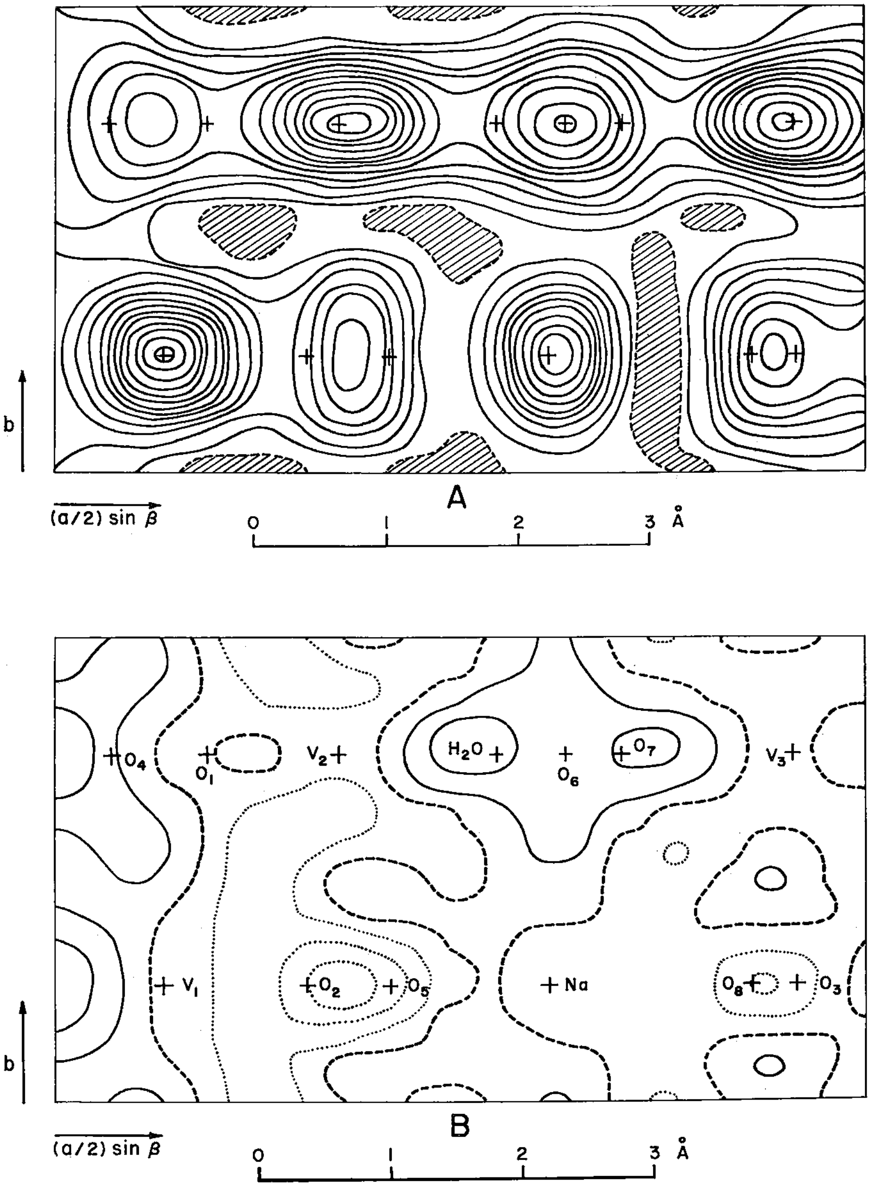

FIG. 2. $Na_2V_6O_{16}.2H_2O$: (A) final electron-density projection along [001] with contours at intervals of 1 $e.Å^{-2}$, and negative areas shaded; (B) final (F_o-F_c)-synthesis projected along [001] with contours at intervals of 0.5 $e.Å^{-2}$, zero contour broken, and negative contours dotted.

tions are replaced by the corresponding $|F_c|$ values, and 0.34 when the unobserved reflections (assuming $|F_o| = 0$) are then included. It may be noted that these values of R become 0.47, 0.29, and 0.52, respectively, if H_2O is omitted from the structure factor calculations. Values of $|F_o|$ and F_c for the $\{hk0\}$ zone of $Na_2V_6O_{16}.2H_2O$ (where Na_2 is to be considered as probably $NaCa_{0.5}$) are listed in Table 4. Final values for the fractional atomic co-ordinates, x and y, are given in Table 5.

Because of the slight ellipticity, with major axes along y, of the contours around some of the atomic positions in Fig. 2, a test was made of

TABLE 4. STRUCTURE FACTOR DATA FOR THE $\{hk0\}$ ZONE OF $NaCa_{0.5}V_6O_{16}.2H_2O$ (F_c for $Na_2V_6O_{16}.2H_2O$ ($B = 3.0$ Å^2))

$hk0$	$\|F_o\|$	F_c	$hk0$	$\|F_o\|$	F_c
100	<5.3	2.9	810	<13.4	−4.8
200	23.9	19.7	910	19.6	19.5
300	15.4	−34.2	10,10	<14.3	−8.2
400	17.7	4.7	020	>63.8	−137.3
500	22.2	−22.2	120	<11.4	−1.4
600	21.1	21.9	220	<11.7	−9.9
700	<12.4	−6.5	320	14.0	18.3
800	>39.9	−64.4	420	<12.5	−2.9
900	<13.7	−9.0	520	12.9	12.6
10,00	<14.1	−14.8	620	<13.4	−12.6
110	31.7	22.1	720	<13.9	4.6
210	16.3	−15.2	820	32.6	40.9
310	12.7	−12.3	130	13.6	−6.8
410	22.0	−23.4	230	<13.8	4.6
510	13.2	−12.6	330	<14.0	4.4
610	<12.2	−8.4	430	21.2	15.3
710	<12.8	13.5			

TABLE 5. FRACTIONAL CO-ORDINATES OF ATOMS IN $Na_2V_6O_{16}.2H_2O$ (where Na_2 probably should be $NaCa_{0.5}$)

Atom	x		y	z
	$\{hk0\}$	$\{h0l\}$		
V_1	0.067	0.067	1/4	0.170
V_2	0.822	0.822	1/4	0.127
V_3	0.540	0.540	1/4	0.830
Na	0.310	0.303	1/4	0.440
O_1	0.906	0.907	1/4	0.869
O_2	0.158	0.140	1/4	0.892
O_3	0.463	0.475	1/4	0.115
O_4	0.965	0.956	1/4	0.282
O_5	0.194	0.214	1/4	0.173
O_6	0.681	0.682	1/4	0.045
O_7	0.647	0.651	1/4	0.725
O_8	0.437	0.436	1/4	0.670
H_2O	0.726	0.708	1/4	0.360

the effect of refinement of this zone in plane group $pg1$, in which y is not restricted to $\frac{1}{4}$ (or $\frac{3}{4}$). As a result, the y co-ordinates of O_5 and O_8 shifted to 0.310 and 0.190, respectively, and the R-factors dropped by approximately 0.03, 0.02, and 0.01, respectively, from those cited above. In view of the limited accuracy of the intensity measurements, however, these changes are relatively insignificant. Therefore, while recognizing that there may in fact be slight departures from the special positions of $P2_1/m$, existing data appear not to justify reduction to $P2_1$ at the present time.

The electron density projection along [010] of the hydrated specimen was derived from the oscillation photographs. The x, z co-ordinates of Table 1, and the atomic scattering factors and general temperature factor previously employed, were adopted for the initial calculation of structure factors. Nearly all atoms were resolved and the peak previously assigned to H_2O again appeared. Refinement was carried out, as before, with successive Fourier and difference syntheses, and the final maps are shown in Fig. 3. The final R-factors are 0.19 for the observed reflections

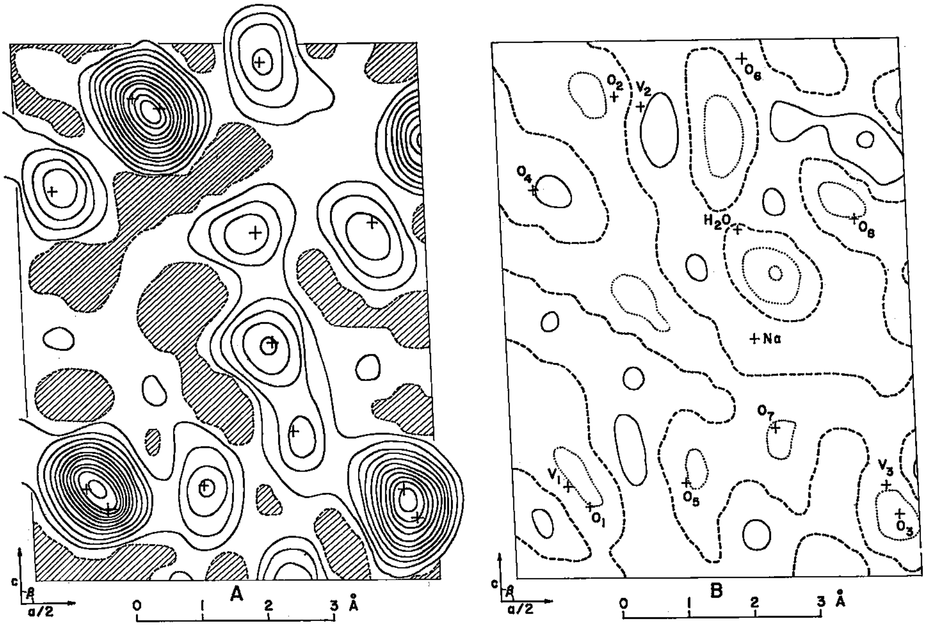

FIG. 3. $Na_2V_6O_{16}.2H_2O$: (A) final electron-density projection along [010] with contours at intervals of 2 e.Å^{-2}, and negative areas shaded; (B) final (F_o-F_c)-synthesis projected along [010] with contours at intervals of 1 e.Å^{-2}, zero contour broken, and negative contours dotted.

only (omitting the twelve strongest reflections), 0.12 when the $|F_o|$'s for these twelve reflections are replaced by the corresponding $|F_c|$ values, and 0.16 when the unobserved reflections (assuming $|F_o| = 0$) are then included. Values of $|F_o|$ and F_c for this zone are listed in Table 6, and final values for the fractional atomic co-ordinates x and z are included in Table 5.

TABLE 6. STRUCTURE FACTOR DATA FOR THE $\{h0l\}$ ZONE OF $NaCa_{0.5}V_6O_{16}.2H_2O$ (F_c for $Na_2V_6O_{16}.2H_2O$ ($B = 3.0$ Å^2)).

$h0l$	$\|F_o\|$	F_c	$h0l$	$\|F_o\|$	F_c	$h0l$	$\|F_o\|$	F_c
001	>50.3	85.6	403	37.5	−27.1	$\bar{2}02$	>45.2	−60.5
002	>32.2	−51.7	404	20.5	11.4	$\bar{2}03$	37.9	−33.7
003	>46.7	−79.7	405	22.9	24.3	$\bar{2}04$	<14.5	− 4.5
004	>34.8	−65.5	500	32.6	−38.4	$\bar{2}05$	<16.4	−4.9
005	<16.7	−5.8	501	29.7	−39.2	$\bar{3}01$	21.9	−20.2
100	<5.6	1.4	502	>41.0	−100.3	$\bar{3}02$	>31.8	75.5
101	19.6	19.8	503	27.7	−22.3	$\bar{3}03$	>41.0	65.6
102	<9.8	−3.5	504	30.7	40.5	$\bar{3}04$	18.3	19.7
103	<12.0	4.3	600	17.6	15.8	$\bar{3}05$	20.5	−17.3
104	36.9	34.0	601	33.3	17.6	$\bar{4}01$	13.7	13.6
105	24.0	−16.9	602	27.6	30.2	$\bar{4}02$	21.3	10.6
200	21.5	20.5	603	<17.4	9.6	$\bar{4}03$	24.0	13.8
201	34.2	40.3	604	<18.9	−18.0	$\bar{4}04$	19.3	−13.7
202	37.6	−32.1	700	<15.8	−9.8	$\bar{5}01$	46.1	47.7
203	23.8	−15.7	701	19.9	−23.2	$\bar{5}02$	>45.7	78.1
204	<15.0	−1.7	702	32.0	23.9	$\bar{5}03$	33.5	39.3
205	17.4	14.2	703	22.7	29.4	$\bar{5}04$	36.7	−35.3
300	33.6	−29.4	800	61.5	−60.2	$\bar{6}01$	<14.5	3.8
301	>50.8	−103.8	801	21.7	35.9	$\bar{6}02$	<15.2	3.8
302	42.0	−50.2	802	32.8	42.3	$\bar{6}03$	<16.3	−4.0
303	38.8	44.1	$\bar{1}01$	30.1	31.8	$\bar{6}04$	<17.8	12.0
304	>39.2	75.0	$\bar{1}02$	16.6	−12.8	$\bar{7}01$	26.4	−21.5
305	30.7	43.8	$\bar{1}03$	39.5	−51.3	$\bar{7}02$	20.0	20.8
400	<11.0	7.1	$\bar{1}04$	>31.8	−52.4	$\bar{7}03$	21.1	15.4
401	35.9	−33.7	$\bar{1}05$	<16.2	1.3	$\bar{8}01$	53.3	−59.9
402	22.4	−20.8	$\bar{2}01$	<8.4	7.4	$\bar{8}02$	21.9	−25.8

DESCRIPTION AND DISCUSSION

The structure of the anhydrous mineral is represented in terms of $Na_2V_6O_{16}$ in Fig. 4. Various bond lengths and other interatomic distances are collected in Table 7.[1]

Each V is surrounded by five O in the form of a distorted trigonal bipyramid. The equatorial triangles of the bipyramids around V_1, V_2, V_3 are defined by O_2, O_4, O_5; O_1, O_6, O_4; O_3, O_7, O_8, respectively, and the associated apices by O_1 (two), O_2 (two), O_3 (two). These atoms are directly

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[1] The x co-ordinates derived from the $h0l$ data (Table 5) were employed in calculating the interatomic distances for the hydrated specimen.

TABLE 7. INTERATOMIC DISTANCES (Å): *A*, IN $Na_2V_6O_{16}$; *B*, IN $Na_2V_6O_{16}.2H_2O$; *C*, IN $\gamma Li_{1+x}V_3O_8$. (Asterisks indicate distances involved in converting trigonal bipyramids to octahedra.)

	No.	*A*	*B*		No.	*A*	*B*		No.	*A*	*B*		No.	*C*
V_1–O_1	2	1.90	1.85	V_2–O_2	2	1.88	1.86	V_3–O_3	2	1.90	1.86	V_1–O_1	2	1.88
V_1–O_2	1	2.28	2.46	V_2–O_1	1	2.21	2.38	V_3–O_3	1	2.27	2.48	V_1–O_1	1	2.06
V_1–O_4	1	1.68	1.67	V_2–O_6	1	1.56	1.82	V_3–O_7	1	1.74	1.64	V_1–O_3	1	1.78
V_1–O_5	1	1.68	1.80	V_2–O_4	1	1.80	2.02	V_3–O_8	1	1.56	1.78	V_1–O_5	1	1.60
V_1–O_1*	1	2.70	3.06	V_2–O_7*	1	3.26	3.80	V_3–O_6*	1	3.22	2.41	V_1–O_7*	1	2.86
O_1–O_2	2	2.48	2.72	O_2–O_1	2	2.48	2.72	O_3–O_3	2	2.50	2.68	O_1–O_1	2	2.42
O_1–O_4	2	2.81	2.78	O_2–O_6	2	2.56	2.85	O_3–O_7	2	2.64	2.73	O_1–O_3	2	2.72
O_1–O_5	2	2.44	2.34	O_2–O_4	2	2.76	2.54	O_3–O_8	2	2.53	2.70	O_1–O_5	2	2.74
O_2–O_4	1	3.85	3.96	O_1–O_6	1	3.45	3.16	O_3–O_7	1	3.54	3.91	O_1–O_3	1	3.64
O_2–O_5	1	2.04	2.42	O_1–O_4	1	2.89	3.38	O_3–O_8	1	2.48	3.62	O_1–O_5	1	3.00
O_4–O_5	1	3.23	3.32	O_4–O_6	1	3.13	3.80	O_7–O_8	1	3.23	2.65	O_3–O_5	1	2.74
O_1–O_1*	2	3.03	3.54	O_2–O_7*	2	3.41	4.33	O_3–O_6*	2	3.30	2.89	O_1–O_7*	2	3.07
O_1–O_2*	1	3.03	2.86	O_1–O_7*	1	3.20	3.30	O_3–O_6*	1	2.86	2.62	O_1–O_7*	1	3.05
O_1–O_4*	1	2.89	3.38	O_6–O_7*	1	2.90	2.61	O_6–O_7*	1	2.90	2.61	O_7–O_3*	1	2.74
Na–O_5	1	2.17	2.38	H_2O–V_2	1	—	2.40	V_1–V_2	1	2.95	3.01			
Na–O_7	2	2.58	2.32	H_2O–Na	2	—	2.42	V_1–V_2	1	3.32	3.34			
Na–O_8	1	2.97	2.42	H_2O–O_8	2	—	2.52	V_3–V_3	2	3.36	3.46			
Na–H_2O	2	—	2.42	H_2O–O_6	1	—	2.56	V_1–Na	1	3.41	3.55			
								V_2–Na	2	4.45	4.28			
								V_3–Na	2	3.57	3.47			

comparable with O_1, O_3, O_5 and O_1 (two) around V_1 in $\gamma Li_{1+x}V_3O_8$ (Wadsley, 1957), and with $O_1(1)$, O_3, $O_2(1)$ and $O_2(2)$, $O_2(3)$ around V in V_2O_5 (Bachmann, Ahmed & Barnes, 1961), and with those of similar polyhedra in other vanadium bronzes, and in the hydrated metavanadates (*e.g.*, Kelsey & Barnes, 1960; Evans, 1960; Bachmann & Barnes, 1961). All of these trigonal bipyramids share edges from the apices to one corner of the equatorial triangle to form continuous zigzag double chains. In the present structure the shared edges are O_3-O_3 (two) between V_3 bipyramids and O_1-O_2 (two) between V_1,V_2 bipyramids, and the chains extend along the direction of y (see Fig. 4). The shared edges (O_1-O_2, O_2-O_1, O_3-O_3; two each) generally are shorter than others of the trigonal bipyramids, and V is displaced away from them so that its distance from that corner of the equatorial triangle which is common to a pair of shared edges is lengthened (V_1-O_2, V_2-O_1, V_3-O_3), while those to the other two corners are shortened (V_1-O_4, V_1-O_5; V_2-O_6, V_2-O_4, V_3-O_7, V_3-O_8). The double chains of V_1,V_2 bipyramids share corners (O_4,O_4) to form spiral tubes around the 2_1 axes along the cell edges perpendicular to the plane $y = 0$. Thus the axes of the chains of VO_5 polyhedra are confined to the planes $z = n$ (where $n = 0, 1, 2, \ldots$); the Na ions interleave these planes and are co-ordinated to O_5, O_7 (two), and O_8 in an irregular tetrahedral array. This arrangement is very similar to that in $\gamma Li_{1+x}V_3O_8$ (Wadsley, 1957), except that Li is surrounded by six O in distorted octahedral co-ordination in the latter, and the oxygen co-ordination polyhedra around V_2 and V_3 (corresponding to the present V_1 and V_2, respectively) take the form of octahedra. In the present structure such octahedral co-ordination would require the addition of O_1 to V_1 and O_7 to V_2, with O_7 then becoming a shared corner with the trigonal bipyramid around V_3 (compare Fig. 4 with Fig. 3 of Wadsley, 1957, after interchanging a and c in the latter). The V-O polyhedra in the lithium vanadium bronze, therefore, are linked into sheets with $z = 0$ as the median plane whereas they occur as separate single and double strings in the metahewettite. This is in qualitative agreement with the fact that the lithium vanadium bronze forms robust, bluish-black needles (Wadsley, 1957), while the metahewettite occurs as soft, friable, long, very thin, red blades.

The accuracy attained in the present structure investigation is not very high, owing to the unsuitable nature of the available material. Thus the interatomic distances (Table 7) found for the anhydrous specimen certainly cannot be accurate to better than 0.1 Å, and those for the hydrate are even less certain. The R-factors, however, are reasonable, and the principal features of the proposed structure are plausible. Nevertheless, $|\Delta F| = ||F_o| - |F_c||$ for several individual reflections (see

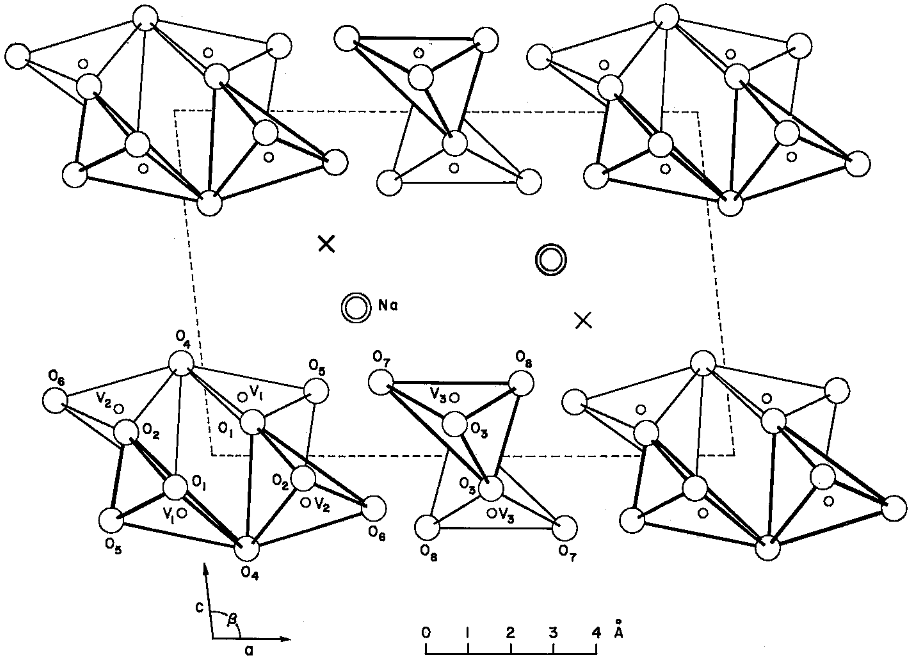

FIG. 4. Projection of the structure of $Na_2V_6O_{16}$ along [010]; the Na sites probably are occupied by approximately equal numbers of Na and $\frac{1}{2}$Ca; the approximate positions of the water molecules in $Na_2V_6O_{16}.2H_2O$ are indicated by crosses.

particularly Tables 2 & 4) is much larger than normally would be tolerated, and the number of independent *hk*0 reflections observed for the hydrated specimen (Table 4) is very small. On the other hand, there is a fair measure of agreement between the individual interatomic distances within the V_3 trigonal bipyramids in the anhydrous specimen and corresponding values in the lithium vanadium bronze (Table 7), and comparable distances are found in the trigonal bipyramids around V_1 and V_2. It may be noted, however, that O_5 is obviously too close to O_2 (2.04 Å) and to Na (2.17 Å), so that it is possible that its true position may be nearer O_4, or that its y co-ordinate, as mentioned previously in connection with the $\{hk0\}$ zone of the hydrated material, may differ slightly from $\frac{1}{4}$; the latter, of course, would reduce the space group to $P2_1$. Other suspiciously short interatomic distances (not listed in Table 7) are O_5-O_7 (two, 2.41 Å) and O_6-O_8 (two, 2.26 Å). It may be noted that, if $y = 0.310$ for O_5 and $y = 0.190$ for O_8, some of the interatomic distances involving these oxygen atoms are improved but others become even less plausible.

In the case of the less accurately determined structure of the hydrated specimen, the short V_3-O_6 (2.41 Å) and V_2-H_2O (2.40 Å) distances (Table 7), if real, would convert the trigonal bipyramidal co-ordination polyhedra around V_3 and V_2 into octahedra (see Fig. 4) with O_3 (three), O_6, O_7, O_8 around V_3, and O_2 (two), O_1, O_4, H_2O, O_6 around V_2, but would leave the trigonal bipyramid around V_1 unchanged. Conversion of the trigonal bipyramids around V_3 and V_2 into octahedra would involve removal of the edges O_3-O_7 (3.91 Å) and O_1-O_6 (3.16 Å), and the addition of O_3-O_6 (two, 2.89 Å), O_3-O_6 (2.62 Å), and O_6-O_7 (2.61 Å) in the first case, and O_2-H_2O (two, 3.34 Å), O_6-H_2O (2.56 Å), and O_4-H_2O (3.13 Å) in the second case. Furthermore, the two O_5-O_7 (2.55 Å) distances, as in the structure of the anhydrous specimen, appear to be rather short. Finally, the V_2-H_2O distance (2.40 Å) would imply that H_2O is co-ordinated both with V_2 and with two Na in addition to O_8 (two) and O_6; such co-ordination is extremely unlikely. Thus, although there is no doubt that the structures of the hydrated and anhydrous specimens are essentially alike and that the actual sites of the H_2O molecules in the former must be close to those found in the present investigation, some adjustments of the atomic parameters, particularly in the hydrate, appear to be necessary. No figure for the structure of the hydrated material, therefore, is given but the approximate positions of the H_2O molecules are indicated by crosses in the projection of the structure of the anhydrous specimen in Fig. 4.

Although the results of the present investigation leave something to be desired, they do represent the first attempt at a complete solution of a structure of the hewettite-metahewettite type. Work on hewettite, metahewettite, and the sodium analogue of the latter is to be resumed in the near future.

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REFERENCES

BACHMANN, H. G., & BARNES, W. H. (1961): Bonding in the trigonal bipyramidal co-ordination polyhedra of V_2O_5 and of certain other structures containing pentavalent vanadium, *Zeits. Krist.*, **115**, 215–230.

BACHMANN, H. G., AHMED, F. R., & BARNES, W. H. (1961): The crystal structure of vanadium pentoxide, *Zeits. Krist.*, **115**, 110–131.

BARNES, W. H. (1955): "Hewettite" and "metahewettite," *Am. Mineral.*, **40**, 689–691.

——— & QURASHI, M. M. (1952): Unit cell and space group data for certain vanadium minerals, *Am. Mineral.*, **37**, 407–422.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H., & VEENENDAAL, A. L. (1955): New calculations of atomic scattering factors, *Acta Cryst.*, **8**, 478–483.

DITTE, A. (1888): Recherches sur le vanadium, *Ann. Chim. Phys.*, (sér. 6) **13**, 190–271.

EVANS, H. T., JR. (1960): Crystal structure refinement and vanadium bonding in the metavanadates KVO_3, NH_4VO_3 and $KVO_3.H_2O$, *Zeits. Krist.*, **114**, 257–277.

——— & GARRELS, R. M. (1958): Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits, *Geochim. et Cosmochim. Acta*, **15**, 131–149.

FOSHAG, W. F., & HESS, F. L. (1927): Rossite and metarossite; two new vanadates from Colorado, *Proc. U.S. Nat. Museum*, **72**, art. 11.

GUITER, H. (1941): Contribution à l'étude des vanadates, *Ann. Chim.*, (sér. 11), **15**, 5–32.

HAUER, K. R. VON (1860): Ueber einige Verbindungen der Vanadinsäure, *J. prakt. Chem.*, **80**, 324–333.

HENRY, N. F. M., LIPSON, H., & WOOSTER, W. A. (1951): *The Interpretation of X-ray Diffraction Photographs*, Macmillan, London.

HEWETT, D. F. (1910): Vanadium-deposits in Peru, *Trans. Am. Inst. Mining Engrs.*, **40**, 274–299.

HILLEBRAND, W. F., MERWIN, H. E., & WRIGHT, F. E. (1914): Hewettite, metahewettite and pascoite, hydrous calcium vanadates, *Proc. Am. Phil. Soc.*, **53**, 31–54.

KELSEY, C. H., & BARNES, W. H. (1960): The crystal structure of metarossite, *Can. Mineral.*, **6**, 448–466; (1961): *loc. sit.*, **6**, 697.

MANASSE, O. (1887): Beiträge zur Kenntniss vanadinsauer Salze, *Liebig's Ann. Chem.*, **240**, 23–61.

MARVIN, R. (1955): CaO-V_2O_5-H_2O system (abstract), *Am. Mineral.*, **40**, 326.

NORBLAD, J. A. (1873): Bidrag till Kännedomen om vanadiums amfidsalter, *Upsala Universitets Årsskrift*; (1875): Sur quelques sels de vanadium (abstract), *Bull. Soc. Chim.*, (nouvelle sér.), **23**, 64–70.

QURASHI, M. M. (1954): On the completion and extension of the table of atomic scattering factors published by Viervoll and Ögrim, *Acta Cryst.*, **7**, 310–312.

——— (1961): The polymorphism and hydration characteristics of hewettite and metahewettite, *Can. Mineral.*, **6**, 647–662.

ROSS, M. (1959): Mineralogical applications of electron diffraction. II. Studies of some vanadium minerals of the Colorado Plateau, *Am. Mineral.*, **44**, 322–341.

WADSLEY, A. D. (1957): Crystal chemistry of non-stoichiometric pentavalent vanadium oxides: crystal structure of $Li_{1+x}V_3O_8$, *Acta Cryst.*, **10**, 261–267.

WEEKS, A. D., & THOMPSON, M. E. (1954): Identification and occurrence of uranium and vanadium minerals from the Colorado Plateau, *U.S. Geol. Survey Bull.*, **1009-B**, 13–62.

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